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VOL. 20, SEC. A. JANUARY, 1942 NUMBER 1

ROTATIONAL STRUCTURE OF THE BIRGE-HOPFIELD BANDS OF N_2[1]

BY J. W. T. SPINKS[2]

Abstract

The 2–10, 3–11, 4–12, 5–13, 5–14, and 6–14 bands of the $a^1\Pi_u \rightarrow X^1\Sigma_g^+$ system in N_2 (Birge-Hopfield bands) have been photographed and measured. P, Q, and R branches are recorded and the indentification of the transition as $^1\Pi \rightarrow {}^1\Sigma$ is definitely confirmed. B', B'', α', and α'' values are presented.

Introduction

Molecular nitrogen has a strong system of bands in the Schumann region, and this system has been identified as a $^1\Pi_u - {}^1\Sigma_g^+$ transition (1, 2, 4). Such bands should show P, Q, and R branches, but, so far, measurements of R lines have not been recorded and, as a result, the certainty of the assignment of these bands to a $^1\Pi_u - {}^1\Sigma_g^+$ transition has been questioned.

The P, Q, and R branches in question showed up very clearly in some plates of the Birge-Hopfield system taken some time ago, and consequently it was thought worth while to record the results of measurements on these plates.

Experimental

Nitrogen from a cylinder was excited in a discharge tube of the type used for producing an intense hydrogen continuum. The photographs were taken in the third order of the 3-metre grating at the Physikalisches Institute in Darmstadt. Interference by the second order of the strong second positive group of nitrogen was eliminated by a semicylindrical quartz lens mounted in front of the slit of the spectrograph and used as a prism.

Hilger Schumann plates were used.

As usual the spectrum of the iron arc was employed as comparison spectrum and the plates were measured with an Abbé comparator.

Results

Rotational analyses of the 2–10, 3–11, 4–12, 5–13, 5–14, and 6–14 bands have been made. There is a good deal of overlapping in some of the bands, and it is usually impossible to separate the R branch lines in the head of the band. As would be expected, the branch lines show alternating intensities. The Q branch is much more strongly developed than the P and R branches,

[1] *Manuscript received October 14, 1941.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

[2] *Professor of Physical Chemistry.*

and in most cases was measured to beyond $Q(40)$. Application of combination differences indicates that the Λ doubling in the $^1\Pi$ state is very small. Assignments of line frequencies are given in Tables I, II, and III.

TABLE I

WAVE NUMBERS OF THE LINES IN THE $a^1\Pi_u \rightarrow X^1\Sigma_g^+$ N_2 BANDS

J	2–10 band. ν_0 = 50,252.50			3–11 band. ν_0 = 49,821.16		
	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$
2	50,250.5	50,244.7+		49,820.4	49,813.6+	49.829.6+
3		39.5+				
4	47.5	35.2+		17.2+	04.2+	32.9+
5	44.7+		50,264.1+			
6	42.0	23.2+	64.1+	11.4	792.7+	32.9+
7	39.5+	16.7	64.1+	08.4+	85.4+	32.9+
8	35.2+	09.6		04.2+		32.9+
9	30.1+	01.9+		00.0	70.8+	
10	25.7	194.5+		795.1	63.4+	29.6+
11	20.5	86.6+		89.7	55.9+	27.1
12	14.7	77.6+	55.7	83.8	47.5+	24.6
13		67.3	51.8	77.9		
14	01.9+	57.6	48.8	70.8+	27.5	17.2+
15	194.5+	46.7	44.7+	63.4+	16.9	13.6+
16	86.6+	36.2		55.9+	06.4	08.4+
17	77.6+	24.9	35.2+	47.5+	695.4	04.2+
18	69.7	13.1	30.1+	39.2	83.4	797.6
19		00.5	23.2+	29.9		92.7+
20	50.8	87.9		20.1	58.0	85.4+
21	40.8	74.2		10.0	45.0	77.9
22	30.1	60.9		699.4	31.2	70.8+
23	19.2	46.8		88.1		63.4+
24	07.5	32.0	186.6+	76.7	02.8	53.9
25	95.5		77.7+	64.4	587.3	47.5+
26	82.7	01.2		51.9	71.8	35.5
27	69.3			38.8	56.0	25.4
28	56.3	49,968.6		25.5	38.9	13.9
29	42.3	51.0		11.2	22.0	03.2
30	27.8			597.1	04.5	692.4

+ *Refers to lines that are overlapped.*

TABLE II

WAVE NUMBERS OF THE LINES IN THE $a^1\Pi_u \rightarrow X^1\Sigma_g^+$ N_2 BANDS

J	4–12 band. ν_0 = 49,391.50			5–13 band. ν_0 = 48,964.05		
	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$
2	49,390.1+	49,383.8+	49,398.5+	48,962.6+	48,956.5+	48,970.7+
3	88.2				52.1	
4	86.6+	74.1+	401.1+	59.0+	46.6+	
5	83.8+	69.2+		56.5+	41.7+	75.1+
6	80.8	62.6	02.8	53.9+	35.4	75.1+
7	77.8+			49.8+		
8	74.1+	47.5+	01.1+	46.6+	22.3	
9	69.2+	40.8+		41.7+	14.7	
10	64.8	33.5+	398.5+	37.3	07.0	70.7+

TABLE II—*Concluded*

WAVE NUMBERS OF THE LINES IN THE $a^1\Pi_u \leftarrow X^1\Sigma_g^+$ N_2 BANDS—*Concluded*

	4–12 band. v_0 = 49,391.50			5–13 band. v_0 = 48.964.05		
	$Q)J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$
11	49,359.7	49,325.8+	49,396.1	48,932.1+	48,898.3+	48,968.0
12	53.9+	17.2+	93.2	26.3+	90.0+	65.6
13	47.5+	08.6+	90.1+	19.8	81.2+	62.6+
14	40.8+	297.5	86.6+	13.1	70.8	59.0+
15	33.5+	86.3	83.8+	05.7	59.9	53.9+
16	25.8+	76.1	77.8+	898.3+	49.6	49.8+
17	17.2+	65.6		90.0+	38.3	43.9
18	08.6+	53.8	66.8	81.2+	26.9	38.7
19	299.6	41.2		72.2	14.5	32.1+
20	89.9	28.5	53.9+	62.4	01.8	26.3+
21	79.8	14.7	44.8	52.1	788.5	17.8
22	68.9	01.6	39.2	41.7	75.3	11.3
23	58.0	188.1	32.2	30.4	60.8	02.9
24	46.5	73.0	22.6	19.0	46.2	894.2
25	34.0	57.3		06.8	31.1	84.3
26	22.1	42.5	04.3	794.2	15.7	75.7
27				81.3	699.5	65.5
28				67.9	83.2	54.7
29				53.4	66.4	43.7
30				39.3	48.4	32.3

TABLE III

WAVE NUMBERS OF THE LINES IN THE $a^1\Pi_u \rightarrow X^1\Sigma_g^+$ N_2 BANDS

J	5–14 band. v_0 = 47,009.30			6–14 band. v_0 = 48,537.5		
	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$
0						48,541.7
1						44.2
2	47,008.1+	47,002.6+		48,536.1		46.0
3						
4	04.7+	46,993.4				
5	02.6+	87.6	47,021.1+	30.8		49.2+
6	00.2+	81.9		27.7		49.2+
7	46,997.1	74.7+	21.1+	24.6		
8	93.4	69.2+		20.8	48,496.8	
9	89.0	62.6+		16.0	89.3	
10	84.9+	54.2	18.2	11.8	81.4	
11	79.5+	46.6	16.0	06.3		
12	74.7+	38.2	13.9	00.5		39.9
13	69.2	29.4	11.2	494.1		
14	62.6+	20.2	08.1+	87.5		
15	55.7	10.3	04.7+	80.2		
15	48.9	00.2	00.2+	72.7		
17	41.1	46,889.4	46,995.4	64.5		
18	33.3	78.7	90.4	55.3		
19	24.6	66.9	84.9+	46.0		
20	15.7	55.1	79.5+	37.2	48,377.0	
21	06.4	43.2	72.7	25.0		
22	896.6	29.9	66.1	15.2		
23	86.2	17.0	58.6			
24	75.6	02.8	50.9			
25	64.1	788.5				
26	52.7	73.8	34.0			

TABLE IV

COMBINATION DIFFERENCES, $\Delta_1F'(J)$, $v' = 5$ (UPPER STATE)

J	$Q(J+1) - P(J+1)$		$R(J) - Q(J)$	
	5–13 band	5–14 band	5–13 band	5–14 band
3	12.4+	11.3+		
4	14.8+	15.0+		
5	18.5+	18.3+	18.7+	
6		22.4+		
7	24.3+	24.2+		
8	26.9+	26.3+		
9	30.3	30.7+		
10	33.9+	32.9+	33.4+	33.2+
11	36.3+	36.5+	35.9+	36.4+
12	38.6+	39.7+	39.3+	39.2+
13	42.3	42.5+	42.8+	42.0+
14	45.9	45.4	45.9+	45.4+
15	48.6+	48.7	48.2+	49.0+
16	51.7+	51.6	51.5+	51.4+
17	54.3+	54.5	53.9+	54.4
18	57.8	57.7	57.5+	57.2
19	60.6	60.5	59.9+	60.3+
20	63.6	63.2	63.9+	62.8+
21	66.4	66.7	65.7	66.3
22	69.5	69.2	69.6	69.6
23	72.9	72.8	72.6	72.4
24	75.7	75.6	75.2	75.2
25	78.5	78.9	77.5	
26	81.8	81.5	81.5	81.3
27	84.7	84.1	84.1	
28	87.0	87.0	86.8	

+ *Using lines that overlap.*

The numbering was determined by the usual methods (see, for example, (3)). Table IV gives combination differences for the 5–13 and 5–14 bands. The agreement of the $\Delta_1F'(J)$ values indicates that the two bands have the same upper state. The fulfilment of the relation $Q(J+1) - P(J+1) = R(J) - Q(J)$ is illustrated in Table IV for the 5–13 and 5–14 bands and gives a check on the analysis of the bands. The rotational constants B_v were obtained from the combination differences in the usual manner, using Q–P differences. The rotational constant, D, was calculated from the equations below, using preliminary B's.

$$D_v = D_e + \beta(v + \tfrac{1}{2}): \quad D_e = \frac{-4B_e^3}{\omega_e^2}$$

$$\beta = \frac{\alpha^2}{6\omega_e} + D_e\left(\frac{8\omega_e X_e}{\omega_e} - \frac{5\alpha}{B_e}\right)$$

$$\omega_e'' = 2359.60: \quad \omega_e' = 1692.28$$

$$\omega_e X_e'' = 14.45: \quad \omega_e X_e' = 13.32$$

$$D_e' = -6.208 \times 10^{-6}: \quad \beta' = 9.54 \times 10^{-8}$$

$$D_e'' = -5.820 \times 10^{-6}: \quad \beta'' = 0.362 \times 10^{-8}$$

TABLE V

ROTATIONAL CONSTANTS

Band	Upper state, $a^1\Pi_u$		Lower state, $X^1\Sigma_g^+$	
	B'_v, cm.$^{-1}$	D'_v, cm.$^{-1}$(calc.)	B''_v, cm.$^{-1}$	D''_v, cm.$^{-1}$(calc.)
2–10	1.579	-5.97×10^{-6}	1.821	-5.78×10^{-6}
3–11	1.551	-5.87×10^{-6}	1.790	-5.78×10^{-6}
4–12	1.538	-5.78×10^{-6}	1.780	-5.78×10^{-6}
5–13	1.521	-5.68×10^{-6}	1.758	-5.77×10^{-6}
5–14	1.522	-5.68×10^{-6}	1.744	-5.77×10^{-6}
6–14	1.507	-5.58×10^{-6}	1.737	-5.77×10^{-6}

The B values are presented graphically in Fig. 1. The results of Appleyard and of Watson and Koontz (taken from their graph) are included. From the figure, $\alpha' = 0.022$ and $\alpha'' = 0.018$. The large number of R branch lines measured confirms the identification of the system as $a^1\Pi_u \rightarrow X^1\Sigma_g^+$.

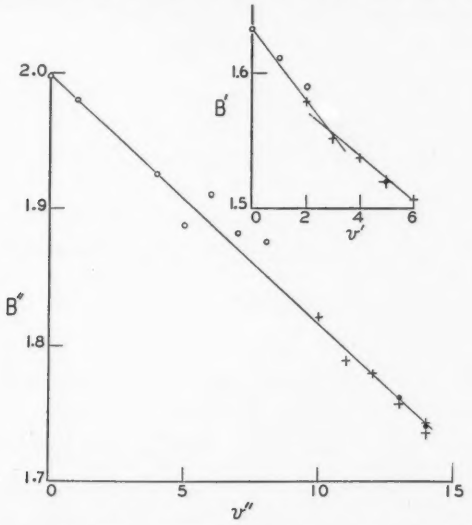

FIG. 1. *B_v vs. v curves for $a^1\Pi_u$ and $X^1\Sigma_g^+$ states of N_2: +, the writer's data; ●, Appleyard's data; ○, data of Watson and Koontz.*

Acknowledgments

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THE VARIANCES OF THE MEANS AND THE VARIANCE OF THE SLOPE OF THE LINE OF RELATION OF A LINEAR, COMPOSITE, BIVARIATE DISTRIBUTION[1]

By F. Charnley[2]

Abstract

The variances of the means and the variance of the slope of the line of relation of a linear, composite, bivariate distribution, in which the variances and correlation coefficient of the component populations remain constant, are analogous to the corresponding variances of a linear regression line. The variances of the means are respectively, $\frac{\sigma_x^2}{N}$, $\frac{\sigma_y^2}{N}$, and the variance of the slope of the line of relation is $\frac{S_{YL}^2}{N(S_X^2 - \sigma_x^2)}$, where σ_x^2, σ_y^2 are the variances of the component populations, S_{YL}^2 is the vertical variance of the composite distribution around the line of relation, N is the total number of measures, and S_X^2 is the variance of the composite distribution around the Y-axis.

The variances of the means and the variance of the slope, m, of the line of relation of a linear, composite, bivariate distribution (1) that are needed in testing the significance of the differences in two lines of relation are entirely analogous to those of the corresponding parameters in a linear regression equation. In view of this close similarity the required variances might therefore be written down by inspection. They are, however, very easily deduced as follows.

Variances of Means

To find the variance in the mean, M_Y, of the composite distribution we need consider only the vertical deviations in the individual means of the component populations. The variance in the mean of a sample of n drawn from a single component population is $\frac{\sigma_y^2}{n}$. Hence, if there are k component populations and a sample of n is drawn from each component, the variance in the mean of the means of the samples will be

$$\frac{k\sigma_y^2}{k^2 n} = \frac{\sigma_y^2}{kn}.$$

If the n's differ, the variance will be

$$\sigma_y^2 \frac{\sum_1^k n_i}{\left(\sum_1^k n_i\right)^2} = \frac{\sigma_y^2}{\sum_1^k n_i}.$$

[1] *Manuscript received September 25, 1941.*

Contribution from the Canned Salmon Inspection Laboratory, Department of Fisheries, Vancouver, B.C.

[2] *Chief Chemist.*

Accordingly, in terms of single measures the variance in the mean of the Y-variate of a linear, composite, bivariate distribution is $\frac{\sigma_y^2}{N}$, where $nk = \Sigma n_i = N$ = the total number of measures. And similarly, the variance in the mean of the X-variate is $\frac{\sigma_x^2}{N}$.

Variance of Slope of Line of Relation

From the equation giving the value of m we have

$$m = \frac{\lambda'}{\lambda},$$

where λ' and λ are the respective standard deviations of the means around the means of the composite distribution. If δm is an error in m, then

$$\begin{aligned} \delta m &= \frac{\partial m}{\partial \lambda'}\,\delta\lambda' + \frac{\partial m}{\partial \lambda}\,\delta\lambda \\ &= \frac{\delta\lambda'}{\lambda} - \frac{\lambda'}{\lambda^2}\,\delta\lambda \\ &= \frac{1}{\lambda}\,(\delta\lambda' - m\delta\lambda). \end{aligned}$$

The square of the error in m is therefore

$$(\delta m)^2 = \frac{1}{\lambda^2}\left[(\delta\lambda')^2 - 2m\delta\lambda\delta\lambda' + m^2(\delta\lambda)^2\right].$$

Summing all the errors and dividing by the number of errors we thus obtain

$$\sigma_m^2 = \frac{1}{\lambda^2}\left[\sigma_{\lambda'}^2 - 2mr\sigma_\lambda\sigma_{\lambda'} + m^2\sigma_\lambda^2\right],$$

in which r is the correlation between the errors in λ and λ'.

Suppose now we draw samples of n from one population. We obtain means $y_{i1}, y_{i2}, \ldots . y_{ij}, \ldots$ These have errors $d_{i1}, d_{i2}, \ldots d_{ij}$. If y_i is the true mean of this population, the squares of the means of the samples are: $y_{i1}^2 = (y_i + d_{i1})^2$, $y_{i2}^2 = (y_i + d_{i2})^2 \ldots .$ The errors in the squares are therefore

$$\begin{aligned} \delta y_{i1}^2 &= y_{i1}^2 - y_i^2 = 2y_i d_{i1} + d_{i1}^2 \\ \delta y_{i2}^2 &= y_{i2}^2 - y_i^2 = 2y_i d_{i2} + d_{i2}^2, \text{ etc.} \end{aligned}$$

If $d_{i1}, d_{i2}, \ldots d_{ij} \ldots$, are small relative to the mean, y_i, which will be true if large samples of n are drawn from this population, $d_{i1}^2, d_{i2}^2, \ldots .$ may be neglected in comparison with $2y_i d_{i1}, 2y_i d_{i2}, \ldots .$ Accordingly, the variance of the square of the average of a sample of n is

$$\overline{(\delta y_i^2)^2} = 4y_i^2\bar{d}_i^2 = 4y_i^2\,\frac{\sigma_y^2}{n}.$$

But λ'^2 is the mean of the squares of k averages, each squared average having the variance $4y_i^2\,\frac{\sigma_y^2}{n}$, if the samples drawn from the individual populations

are each of size n. Hence, the variance of the sum of the squared averages is $4\sum_1^k y_i^2 \frac{\sigma_y^2}{n}$ and that of the mean of the squared averages

$$4\Sigma y_i^2 \frac{\sigma_y^2}{nk^2} = 4\frac{\sigma_y^2}{nk}\lambda'^2 = \sigma_{\lambda'^2}^2.$$

To find the variance of λ' from this last equation we note that

$$\delta\lambda'^2 = \frac{d\lambda'^2}{d\lambda'}\delta\lambda' = 2\lambda'\delta\lambda'$$

and, consequently,

$$\overline{(\delta\lambda'^2)^2} = 4\lambda'^2\overline{(\delta\lambda')^2} = \sigma_{\lambda'^2}^2 = \frac{4\sigma_y^2}{nk}\lambda'^2,$$

giving

$$\overline{(\delta\lambda')^2} = \sigma_{\lambda'}^2 = \frac{\sigma_y^2}{nk}.$$

The variances of λ' and λ, the standard deviations of the different means around the means of the composite distribution, are thus merely the variances of the individual means divided by the number of component populations. Furthermore, since the correlation between averages of samples of n drawn from a single population is the same as the correlation between single measures (Appendix), the correlation between the errors in λ and λ' must also be r, the correlation between single measures in the individual populations. The required variance of m, the slope of the line of relation, is accordingly,

$$\sigma_m^2 = \frac{\sigma_y^2 - 2mr\sigma_x\sigma_y + m^2\sigma_x^2}{nk(S_X^2 - \sigma_x^2)}$$

or

$$\sigma_m^2 = \frac{S_Y^2 - 2mp_{XY} + m^2S_X^2}{N(S_X^2 - \sigma_x^2)},$$

in which S_X^2, S_Y^2 are the respective variances of the two variates of the composite distribution around the means of these variates, and N is the total number of measures.

The form of the last equation shows that the variance of m is a quadratic function of m, that it is independent of the nature of the point set representing the means of the component distributions, and that it is applicable to any linear, composite, bivariate distribution. The preceding equation, on the other hand, shows that the equation giving the variance of the slope of a linear regression line (2) is merely the special case of this equation obtained on writing $\sigma_x = 0$.

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APPENDIX

Let samples of n be drawn from a bivariate population in which two characters X and Y are correlated with correlation r. If averages of the two variates in samples of n are correlated, the means of the two distributions will evidently remain the same. Let deviations be taken from the respective means and let

$$u_1 = \frac{x_{11} + x_{12} + - - + x_{1n}}{n}, \quad v_1 = \frac{y_{11} + y_{12} + - - - + y_{1n}}{n}$$

$$- -$$

$$u_N = \frac{x_{N1} + x_{N2} + - - - + x_{Nn}}{n}, \quad v_N = \frac{y_{N1} + y_{N2} + - - - + y_{Nn}}{n}.$$

Then $\sigma_u = \frac{\sigma_1}{\sqrt{n}}$, $\sigma_v = \frac{\sigma_2}{\sqrt{n}}$, and $\bar{r} = \frac{\Sigma uv}{N\sigma_u\sigma_v}$, where $\bar{r}$ is the correlation between the averages in the samples of n.

Substituting the values of u and v in the product term we have

$$\Sigma uv = u_1v_1 + u_2v_2 + - - - - + u_Nv_N.$$

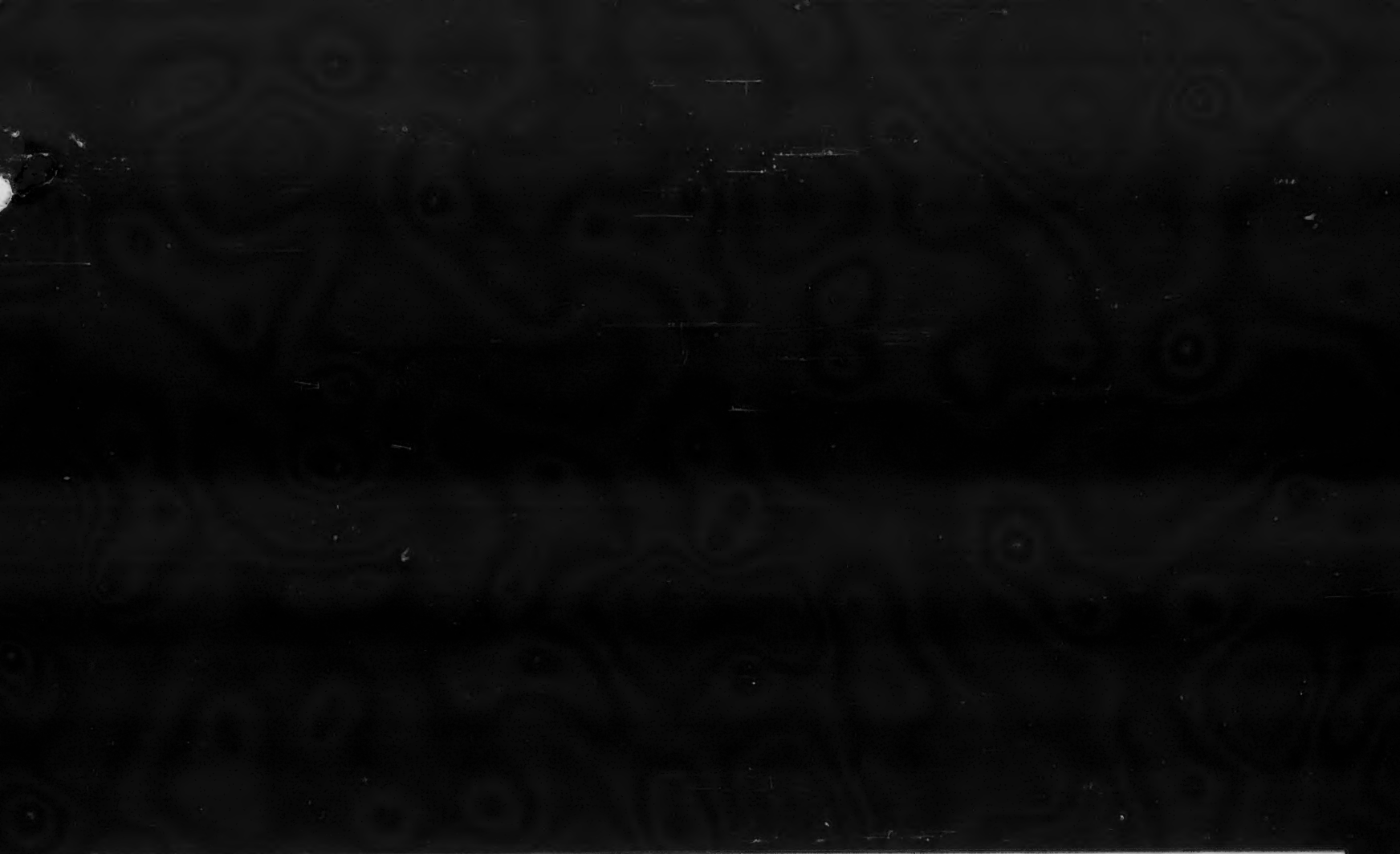
$$\begin{aligned} n^2\Sigma uv &= (x_{11} + x_{12} + - - - + x_{1n})(y_{11} + y_{12} + - - - + y_{1n}) \\ &\quad + (x_{21} + x_{22} + - - - + x_{2n})(y_{21} + y_{22} + - - - + y_{2n}) \\ &\quad + - - - - - - - - - - - - - - - - - - - \\ &= x_{11}y_{11} + x_{12}y_{12} + - - - + x_{1n}y_{1n} + x_{21}y_{21} + x_{22}y_{22} \\ &\quad + - - - - - - - + x_{2n}y_{2n} + - - - + \text{products in which the} \end{aligned}$$

independent variate of a given pair in a sample is associated with the dependent variates of other pairs in the sample. By a slight extension of the product theorem* the sum of the latter must be zero. Hence

$$n^2\Sigma uv = \Sigma xy,$$

where x and y are corresponding values in single samples. Accordingly,

$$\bar{r} = \frac{\Sigma xy}{n^2}\,\frac{n}{N\sigma_1\sigma_2} = \frac{\Sigma xy}{Nn\sigma_1\sigma_2} = r,$$

since the total number of measures is Nn.

*KELLEY T. L. Statistical method. The Macmillan Company, New York. 1923.